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## STUDIES ON THE EFFECT OF NONTANS IN VEGETABLE TANNING

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Wattle (*Acacia mollissima*), babul (*Acacia arabica*), goran (*Ceriops roxburghiana*) and myrobalan (*Terminalia chebula*) extracts were investigated. In the case of purified extracts and gum free extracts, the penetration through the pelts was the maximum and the least with the original and gum added purified extracts in all cases. The leathers tanned with gum free aqueous extracts contained less fixed tannin than the corresponding aqueous extracts. The shrinkage temperature was maximum in the case of leathers tanned with purified and minimum when tanned with the gum free aqueous extracts.

Nonphenolic nontans like acids, salts, gums and sugars of vegetable tan liquors play a very important role in vegetable tanning. Acids and salts are known to affect the collagen fibre structure and to modify the properties of vegetable tan liquors,<sup>2-6</sup> thus controlling rate of penetration, fixation of tannins, yield and colour of the leather. Thiry<sup>7</sup> has stated that the salts of weak acids control the pH and displace the stronger acids from combining with collagen. Gums, on the other hand, make the tan liquor more viscous, impairing the penetration of the tannin through the pelt. Cunningham and Ghosh<sup>8</sup> showed that mangrove liquors penetrate through the pelt slowly; and this was attributed by Ghosh and Barat<sup>9</sup> due to more of gum content in tan liquors. It has been reported that some of the outstanding differences between the tanning materials lie in their differences in salt and acid content, their acid-salt ratio and character of nontans.

The tannin also in most of the cases is a mixture of compounds of varying degree of complexity and with varying ability to combine with the hide protein; so the behaviour of such an infusion towards pelt immersed in it depends to a large extent on the relative balance of all the constituents.

The present work was designed to determine the properties of the leathers tanned with tan liquors having varying amounts of nonphenolic nontans.

### Experimental

Four different extracts were prepared from each vegetable tannin extract: (i) aqueous extract (prepared from the material without any modification), (ii) purified extract (entire removal of gum and partial elimination of acids and salts by the mixed solvent purification method), (iii) gum added to the purified extract and (iv) gum free extract (re-

removal of gum alone from the original aqueous extract by alcoholic precipitation method without affecting the salts and acids).

#### PREPARATION OF THE EXTRACTS

##### I. Aqueous extracts

A stock solution of goran bark was made by extracting the goran bark thrice at room temperature using 1:3 bark-water for 3 days. The three consecutive extractions were mixed, centrifuged and taken to complete dryness, under reduced pressure. Babul bark extract was also similarly prepared.

Myrobalan nuts were crushed and extracted with cold water for 18 hours in the ratio as 1:3; the resultant infusion was filtered, centrifuged and vacuum distilled. Commercial wattle extract was used as such. All the four extracts were analysed for the tannin, nontannin contents; total salts, acids and gums by the standard method. The results are given in Table 1.

##### II. Purification of the extracts

Isolation of pure tannins in bulk quantities in the strictly organic sense is still a problem as ordinary methods of fractionation are not applicable. It was thought worthwhile to first consider the possible methods of separation of the tannin portion from the associated nontans. Several methods of freeing nontans from tannins viz., lead salt method,<sup>10-13</sup> salting out technique,<sup>14</sup> adsorption with hide power,<sup>15</sup> stripping method, solvent extraction method and dialysis using different membranes etc., have been studied in detail.

In all experiments mixed solvent purification technique was followed which gave good yield.<sup>16</sup> A mixture of 10:1 acetone and methanol was used. The extracts were stirred well with the solvents for 5-10 minutes and allowed to settle. The dissolved tannin was filtered. The extract was again treated with the mixed solvent, repeating the process until the solution became almost colourless. The collected fractions were mixed

Table 1  
ANALYSIS OF AQUEOUS EXTRACTS

	Goran	Babul	Wattle	Myrobalan
Tan content/100 g. T.S.	69.8	58.1	74.5	71.3
Nontan content/100 g. T.S.	30.2	41.9	25.5	28.7
T/N.T. ratio	2.3	1.38	2.9	2.5
pH	4.6	4.7	4.9	3.3
Gum content/100 g. extract	11.5	7.9	8.0	—
Total salts (meq./100 g. T.S.) (Resin method)	260.6	72.8	50.1	45
Acidity (meq./100 g. T.S.)	65.1	15.8	10.2	280

together, distilled and dried. The dried extracts were subjected to analysis and the results are given in Table 2.

### III. Gum free extracts

Following the method of Roux,<sup>17</sup> 10 g. each of the aqueous extracts except myrobalan was dissolved in a little quantity of water and absolute alcohol added slowly in excess with vigorous stirring. The precipitate obtained was centrifuged. The tannin-alcohol mixture was distilled under reduced pressure and dried. The extracts thus prepared are free from gum but contain acids and salts.

### IV. Gum added purified extracts

The gum is prepared from each of the extracts by adopting Roux's technique. A calculated quantity of gum was added to each of the purified extracts as present in the aqueous extracts.

#### PREPARATION OF TAN LIQUORS

Since ultimate fixation within certain limits would be governed more by the

total amount of tannin present rather than by that of nontans, experiments were conducted on equitan content basis instead of on the basis of equal Bk strength which individually records total solubles only.

Liquors from various extracts were prepared so that each contains tan/pelt ratio as 1:1 and the liquor/pelt ratio as 15:1 and the concentration of tannin was maintained at 6.7%.

#### PREPARATION OF THE PELTS

Delimed and acetone dehydrated cow pelts (approx. 6×6") were used for tanning experiments and 14 equal pieces were taken. The thickness of the pelts was about 3-4 mm. As myrobalan contains no gum, only two experiments were conducted with (a) aqueous extract and (b) purified extract.

The pieces were numbered, weighed and soaked overnight in water. They were then drained, blotted between the filter paper and reweighed quickly before tanning.

Table 2  
ANALYSIS OF PURIFIED EXTRACTS

	Goran	Babul	Wattle	Myrobalan
Tan content/100 g. T.S.	90.8	81.9	93.5	87.2
Nontan content/100 g. T.S.	9.2	18.1	6.5	12.8
T/N.T. ratio	9.9	4.2	14.4	6.8
pH	3.7	3.45	3.5	2.75
Gum content/100 g. extract	—	—	—	—
Total salts meq./100 g. T.S. (Resin method)	96.4	32.7	6.9	6.4
Acid content meq./100 g. T.S.	30.7	8.3	2.8	99.2

**Table 3**  
PENETRATION OF PELTS BY MODIFIED EXTRACTS (%)

	Goran				Babul				Wattle				Myrobalan	
	A	B	C	D	A	B	C	D	A	B	C	D	A	B
2nd day	50	70	30	75	75	75	75	90	50	70	30	75	30	30
4th day	70	80	60	90	complete				80	95	75	95	75	75
5th day	95	com- plete	75	com- plete	complete				95	com- plete	95	com- plete	complete	
6th day	complete		95	com- plete	complete				complete				complete	
7th day	penetration complete													

**Table 4**  
COLOUR OF TANNED PELTS (VISUAL OBSERVATION)

	A	B	C	D
Goran	Dark brown	Brown	Light brown	Light brown
Babul	Light brown	Very light brown	Very light brown	Very light brown
Wattle	Pink (pale)	Light pink	Light	Very light pink
Myrobalan	Dark yellow	Yellow		

**Table 5**  
pH MEASUREMENTS OF EXTRACTS OF LIQUORS

	A	B	C	D
Goran before tanning	4.6	3.7	4.2	4.2
after "	4.4	4.5	4.9	4.9
Babul before tanning	4.7	3.4	3.8	3.8
after "	4.9	4.2	4.5	4.4
Wattle before tanning	4.9	3.5	4.3	4.3
after "	5.5	4.4	5.2	5.0
Myrobalan before tanning	3.3	2.7	—	—
after "	3.4	2.8	—	—

Note: A—Aqueous extract; B—Purified extract; C—Purified extract + gum;  
D—Gum free aqueous extract.

Table 6

## ANALYSIS OF LEATHERS TANNED WITH MODIFIED EXTRACTS

Nature of extract	Babul					Goran					Wattle					Myrobalan				
	W.S.	F.T.	H.S.	D.T.	T <sub>s</sub> (°C)	W.S.	F.T.	H.S.	D.T.	T <sub>s</sub> (°C)	W.S.	F.T.	H.S.	D.T.	T <sub>s</sub> (°C)	W.S.	F.T.	H.S.	D.T.	T <sub>s</sub> (°C)
Aqueous extract	8.3	32.6	45.1	72.4	82	7.9	34.9	43.2	80.7	90	8.0	31.6	46.4	68.1	86	11.2	26.1	48.7	53.4	66
Purified extract	7.1	37.3	41.1	92.0	84	6.6	39.1	40.3	97.0	91	7.5	34.9	43.6	80.9	88	11.0	29.8	45.2	65.9	68
Purified and gum added extract	7.1	38.4	40.5	94.8	90	6.0	40.8	39.2	104.1	90	6.5	40.9	38.6	106.0	88	—	—	—	—	—
Gum free aqueous extract	7.4	30.8	47.8	64.5	82	6.8	32.2	47.0	68.5	89	8.9	30.7	46.4	68.2	85	—	—	—	—	—

W.S.—Water solubles (%); F.T.—Fixed tannins (%); H.S.—Hide substance (%); D.T.—Degree of tannage; T<sub>s</sub>—Shrinkage temperature.

The pelts were then suspended in liquors with thread, occasionally stirred during the day and left closed during night. The pieces were examined every-day for penetration. After 10 days, when penetration of all the pieces was complete, they were taken out and dipped in distilled water twice, wiped with cotton wool and superficially treated with thymol and dried at room temperature without oiling. The colour of the dry leathers was noted and dried weights of the leathers were taken. The pH of the liquors before and after tanning, penetration and colour of tanned pelts are given in Tables 3-5. The leathers so obtained were analysed for their physical and chemical characteristics. The results are given in Table 6.

### Results and Discussion

Aqueous extract of goran contains more salts and myrobalan contains more acids compared to babul and wattle.

In the purified extracts, salts and acids were removed to a considerable extent and the entire removal was not possible even after repeated solvent purifications. In all the cases higher tan fixation was observed in purified extracts presumably due to the purified liquors having lower pH value and salt content than the corresponding aqueous infusions. This is in conformity with the observation made by earlier workers.<sup>18, 19</sup>

In all the cases of purified extracts, pH is considerably lowered, but gum addition to the extract raises the pH and the values are less than the pH of the aqueous extracts. Removal of gum also brings down the pH. It would appear that gum has

a definite role in controlling the pH of the liquors.

The removal of gum resulted in the lowest fixation of tannins whereas the purified extract to which gum was added gave the highest fixation. As the tanning proceeded, the pH value gradually increased in all the cases. It may be explained by the absorption of the free acids and the acidic tannins by the pelt and oxidation of those tannins, which are of condensed type.

The rate of penetration was more in the case of purified and the gum free aqueous extracts. Penetration was slow in gum added extracts. It is obvious from the results that the gum slows down the rate of penetration. The order of penetration was as follows:

Gum free > purified > aqueous > gum added purified.

Penetration was complete on the 4th day in the case of babul and on the 5th day in the case of myrobalan. The rate of penetration was very slow in the case of goran. It has been observed<sup>20</sup> that the slow penetration of goran is due to its high astringency value, low pH and greater average particle size.

It has been shown<sup>21</sup> that high acid and low salt content result in relatively lower  $T_s$ ; this is in agreement with our findings. The shrinkage temperature of myrobalan tanned leathers was lower than that of leathers tanned by other tanning materials. A relation between  $T_s$  and degree of tannage and between  $T_s$  and nontans has been observed by Simoncini.<sup>22</sup> There is no difference in  $T_s$  between the leathers tanned by gum

added purified extracts and gum free aqueous extracts. But the  $T_s$  of the purified extracts was found to be maximum in all the cases. This shows that removal of nontans has a definite bearing on  $T_s$ .

It was observed that the amount of water solubles was more in the aqueous extract than in the purified and gum added purified extracts. Tannin fixation was of the order: gum added purified extracts > purified extracts > aqueous extracts > gum free aqueous extracts. This indicates the important role of gum in the fixation of tannins.

The pelts tanned in the purified, gum added purified and gum free aqueous extracts were of lighter shades as compared to those tanned in aqueous extracts. The solvent purified liquors produced the best colour followed by gum free and gum added purified extracts. The aqueous extracts gave leathers of darker shades. The results showed that the external addition of gum to the purified extracts does not appreciably improve the colour of the final leather.

It may therefore be concluded that the purified extracts i.e., extracts having smaller particle size and less of nontans are found to be the best in so far as the rate of penetration, colour of the tanned pelt,  $T_s$  and degree of tannage are concerned.

#### Acknowledgment

Our thanks are due to the authorities of the United States Department of Agriculture for the grant under PL 480 which made this work possible.

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